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(54) Title: RETROREFLECTIVE INKS AND FABRICS

(57) Abstract: Described is a retroreflective ink adapted for use on fabrics and other substrates. A retroreflective ink includes a non-volatile matrix material, a volatile component, and a plurality of uncoated beads. Also described are methods of printing fabrics with retroreflective inks.

RETROREFLECTIVE INKS AND FABRICS

Field Of The Invention

The invention relates the field of inks suitable for printing onto textiles. More particularly, the invention relates to inks suitable for printing retroreflective patterns onto fabrics.

Background Of The Invention

Retroreflective surfaces redirect light from environmental sources such as automobile headlights and overhead streetlights into the eyes of others. Retroreflectorized objects are therefore more visible under low light conditions than nonreflectorized objects. In order to promote public safety, objects commonly encountered in motor vehicle traffic that are often made retroreflective. For example, traffic signs, emergency response vehicles, vehicle license plates, bicycles, and the like are made retroreflective to make them more conspicuous, especially at nighttime and during inclement weather. In a similar fashion, various articles of clothing are sometimes made retroreflective to make the wearer more visible to others.

Retroreflective compositions for use on fabrics and other objects are known in the art. For example, retroreflective coating compositions are disclosed in Palmquist et al. U.S. Pat. No. 2,963,378; Nellessen, U.S. Pat. Nos. 3,099,637; 3,228,897; and 3,420,597; Longlet et al. U.S. Pat. No. 3,535,019;

Bingham U.S. Pat. Nos. 4,103,060; Re. 30,892; and 4,263,345; Fouche Jr. U.S. Pat. No. 4,187,332; and Rizika et al. U.S. Patent No. 5,650,213. Commercially available retroreflective compositions include SCOTCHLITE textile ink (Minnesota Mining and Manufacturing Co., St. Paul, MN) and ILLUMITE textile ink (Reflective Technologies, Inc., Cambridge, MA).

Conventional retroreflective compositions are useful for rendering various objects more visible. They are, however, expensive and difficult to work with. For example, conventional retroreflective compositions generally comprise translucent beads hemispherically coated with a reflectorizing substance such as metallic aluminum. E.g., Rizika et al. U.S. Patent No. 5,650,213. Such beads are not only relatively costly to manufacture but also result in the retroreflective compositions being unstable. That is, when such beads are dispersed in commonly used liquid carriers, the resulting mixture becomes unusable within a period of a few days. Because this mixture has a relatively short shelf life, conventional retroreflective compositions are sold as two or three separated precursor components. Prior to use, these precursor components must be mixed together to form a retroreflective ink.

Conventional retroreflective compositions are also not optimized for printing onto textiles because they often clog printing screens, require a relatively high curing temperature, and are compatible only for printing onto darker fabrics as the retroreflective compositions themselves typically have a dark gray color. Moreover, many of the available retroreflective compositions are not suitable for use on garments because coating of such compositions onto a fabric often renders the fabric inflexible or rough to the touch.

Summary Of The Invention

A easy to use retroreflective ink has been developed. The components of this ink are stable relative to one another, allowing the ink to be stored for relatively long periods in premixed form. This ink is also adapted for use on garments and is particularly suited for use in automated printing processes.

Accordingly, the invention features a retroreflective ink composed of a multitude of components including a non-volatile matrix material, a volatile component, and a plurality of beads exhibiting retroreflective qualities but not having a reflective coating. In some variations of the foregoing, the beads comprising this ink can have a mean diameter of about 10-40 microns (e.g., about 25 to 35 microns, less than 30 microns, and about 25 microns), can be clear (i.e., transparent or colorless) or tinted to a predetermined color, solid, spherical or nonspherical in shape, and/or comprised of a glass such as silica.

In one aspect of the invention, the beads comprise about 55-60% the ink volume when all of the volatile carrier (e.g., water) has been removed from the ink. In another aspect of the invention, the non-volatile matrix material (e.g.,an acrylic copolymer) comprises about 40-45% of the ink volume when all of the volatile carrier has been removed from the ink. In some embodiments, the volatile component comprises about 45-50% by volume of the ink.

Also within the invention is a retroreflective ink containing numerous components including a non-volatile matrix material, a volatile component, and a plurality of beads, but not containing any pigment particles.

The invention additionally features a fabric having an ink of the invention

thereon. Also within the invention are methods of making a retroreflective fabric, the methods including the step of printing a fabric with a retroreflective ink of the invention.

In another aspect, the invention features a retroreflective ink including a mixture having both 409 AG Reflective Clear LF Base and Grancill PWX Binding and Finishing Agent.

As used herein, the word "retroreflective" is an adjective that indicates that an object or substrate reflects rays of light in directions close to opposite the direction of the incident rays (e.g., along their originating path) with this property being maintained over wide variations of incident ray directions.

As used herein, the word "ink" means a fluid useful for depositing a substance onto a substrate, e.g., a retroreflective composition onto a fabric.

As used herein, an object has a "reflective coating" when it has applied thereon one or more layers of a reflective material such as a metallic material (e.g., aluminum) or a non-metallic material (e.g., an organic compound). For example, spherical beads having with metallic aluminum hemispherically covering their surfaces have a reflective coating.

As used herein, the word "colorless" is an adjective that describes an object having no readily observable tint or hue. For example, common glass having no exogenously added tinting agent or dye is colorless. By "tinted" is meant having an added color or hue. For example, retroreflective beads are tinted when a coloring agent or dye is added to impart a color to the beads.

As used herein, the phrase "pigment particle" means is particulate solid (although not a "spherical bead") which is insoluble in, and essentially physically and chemically unaffected by, the vehicle in which it is incorporated. Typically, pigment particles are used to impart a color in the substance in which they are incorporated.

As used herein, the word "fabric" means a woven material such as a textile. Fabrics can be composed of natural or synthetic materials such as cotton, nylon, polyester and the like, and are often fashioned into garments such as article of clothing.

Unless otherwise defined, all technical terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In the case of conflict, the present specification, including definitions will control. In addition, the particular embodiments discussed below are illustrative only and not intended to be limiting.

Detailed Description

The invention encompasses retroreflective inks comprising a non-volatile matrix material, a volatile component, and a plurality of beads.

Components of the Retroreflective Ink

Beads suitable for use in the compositions of the invention are commercially available. For example, spherical beads are available from Potter's Industries (Valley Forge, PA) and Light Bead (Arlington, MA). In preferred embodiments of the invention, the beads are roughly spherical in shape, composed of glass (e.g., silica), and have a diameter of approximately 10 to 200 microns (e.g., 10, 12, 14, 16, 18, 20, 22, 24, 25, 26, 28, 30, 32, 34, 35, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, or 200 microns). Although the beads can be a heterogenous mixture of beads of varying diameter, in preferred embodiments, the beads are a fairly homogenous mixture of beads having a mean diameter of approximately 25 to 35 microns. For screen printing, preferred embodiments feature smaller beads because smaller beads flow more easily through the pores of the screen mesh and are less apt to cause clogging. The particular mean diameter of the bead can be selected by one of ordinary skill in the art according to the mesh count of the screen. For example, beads having a mean diameter of approximately 25 microns are suitable for use with screens having a mesh count in the range of 110 threads per inch (tpi). Likewise, smaller diameter beads (e.g., 15 to 20 microns) would be suitable for use with finer mesh counts. By varying the

composition of the glass used to make the beads, the beads can have an index of refraction ranging from 1.7 to 2.5. In preferred embodiments, in order to ensure sufficient retroreflectivity, the beads have a mean index of refraction of at least about 1.9 (e.g., 1.9, 2.0., 2.1, 2.2., 2.3, 2.4, 2.5). In preferred embodiments, the beads are translucent and not colored.

In some applications, however, the glass comprising the beads is tinted a particular color so that the beads have a tint (e.g., a red, orange, yellow, green, blue, or violet hue). In preferred embodiments the beads are solid. In other embodiments, however, they can also be hollow, or perforated (e.g., with pores of varying diameter such as 1, 2, 5, 10, 20 microns in diameter).

The beads within the subject invention may have a roughly spherical shape. In alternate embodiments, the beads may have other shapes. For example, the beads may be polygonal, cone-shaped, star-shaped, of an irregular shape, etc. The beads may even comprise a mixture of two or more differently-shaped beads. Preferred shapes of the beads are those that enhance retroreflectivity.

The non-volatile matrix material featured in the invention is any suitable material that facilitates coating of the beads onto a substrate (i.e., the object to which the ink of the invention is applied such as textiles, fabric, paper, leather, plastic, glass, metals, wood, rubber, synthetic rubber, composites, etc.). Suitable compositions for use as the non-volatile matrix material are known in the art. For example, matrix materials typically used in conventional (non-retroreflective) textile inks may be used.

In preferred embodiments, the non-volatile matrix material takes the form of a transparent or translucent non-volatile film-forming emulsion. Exemplary non-volatile matrix materials suitable for use on fabric such as those used to make clothing include, but are not limited to acrylic, vinylidene chloride, butadiene, acrylonitrile or urethane polymers, or any of suitable mixture of the foregoing. Materials suitable for use as or preparation of the non-volatile matrix are commercially available from chemical suppliers such as Sigma-Aldrich (St. Louis, MO). In a particularly preferred embodiment, the non-volatile matrix material is an acrylic copolymer. Still other materials suitable for use as the non-volatile matrix material can be selected by one skilled in the art based on the properties desired for a particular application. For example, various oils, resins, solvents can be used as the non-volatile matrix material in certain applications.

The volatile component of the invention is a liquid component conducive to evaporation. The volatile component can be any suitable liquid or combination of two or more liquids such as volatile organic solvents. Materials suitable for use as or preparation of the volatile component are commercially available from chemical suppliers (e.g., Sigma-Aldrich). In a particularly preferred embodiment, the volatile component is water. Water that has been distilled, deionized, and/or filtered to remove contaminants is preferred. Still other materials suitable for use as the volatile component can be selected by one skilled in the art based on the properties desired for a particular application.

While the foregoing comprise the minimal elements typically needed to fabricate the inks of the invention, other components can be added to the ink

depending on the particular qualities desired. For example, although the preferred inks of the invention are colorless and do not contain insoluble coloring agents such as pigment particles, such particles or, alternatively, soluble coloring dyes can be added to the ink so that a substrate treated with the ink takes on a pre-selected color or hue. Additionally, in certain embodiments, texturizing agents may be added to the inks where it is desired to impart a particular surface quality to the substrate to which the ink is applied. For example, sand particles may be added to the ink so that the substrate to which the ink is applied exhibits a high friction surface. Still other ink additives may be included. These can be selected by one skilled in the art depending on what particulars qualities are desired. For example, to further adapt the inks for use in a screen printing process, materials such as lubricants, surfactants, dispersants, thickeners, defoamers, stretch additives (i.e., agents that impart elasticity), binding agents (i.e., agents that help adhere solid particulates to substrates), finishing agents, low crocking agents, cross link agents (e.g., CX100, Zeneca Industries, Wilmington, MA), low cure additives (i.e., agents that reduce the time and/or temperature of curing), fixers and/or ammonium hydroxide can be added.

Preparation of the Retroreflective Ink

In various preferred embodiments of the invention, the retroreflective ink is prepared for use by mixing the beads, non-volatile matrix material, volatile component, and, optionally, the aforementioned additives together to form an

ink. Appropriate amounts of each of the foregoing components are added together in a predetermined ratio then mixed to form the ink. Mixing can be accomplished by any means known in the art, e.g., using a high speed mixer or blender.

The precise ratio selected will depend on the particular application for which the ink will be used and can be selected by one of skill in the art based on the characteristics of each component. For example, in a particularly preferred embodiment suitable for use in screen printing fabrics, a bead-matrix mixture is prepared where the mixture comprises by volume about 55-60% beads and about 40-45% non-volatile matrix material. The volatile component is added to the bead-matrix material in an amount so that the volatile component is present at about 45-50% the volume of the ink (i.e., the total volume of the beads, matrix material, and volatile component). That is, the volatile component is added to the bead-matrix material mixture in a ratio of about 1:2 by volume.

After mixing the foregoing components together to form the ink, the ink is stored in an airtight container so that the volatile component does not appreciably evaporate prior to use.

Applying Retroreflective Inks to Substrates

The inks of the invention can be applied to substrates by any suitable method known in the art. For example, the inks can by manually applied to a piece of fabric by simply dispensing (e.g., using a pipet) a quantity of the ink onto the fabric. Other suitable methods for applying the inks to a substrate

include coating (e.g., Floating Knife or Knife Over Roll method), stenciling, ink jet printing, and web or rotary screen printing. In commercial processes where a large number of fabric articles to be treated with the inks of the invention, the preferred method of application is screen printing.

In one exemplary embodiment, a rotary screen printing process is used to apply the ink to a substrate. In this method, the ink is pumped into the inner portion of a perforated cylindrical screen and forced out onto a substrate through the tiny screen perforations. The screen perforations can be made in the form of a predetermined image, so that the ink becomes deposited onto the substrate in a repeating pattern of the predetermined image. Thus, for example, where it is desired to render a pre-existing image printed on a fabric retroreflective, a transparent version of the retroreflective ink of the invention is printed directly over the pre-existing image using a screen duplicating the image. To add a retroreflective tint to the image, a dye or coloring agent is added to the retroreflective ink before it is printed onto the image.

Substrates printed with a retroreflective ink of the invention are cured by applying heat for a predetermined period of time to the substrate. The exact amount of heat added and time needed to effect a cure will depend upon the particular retroreflective ink and substrate used. This can be determined without undue experimentation. In a typical application, the temperature of the ink is raised to 325 degrees F. With the addition of low cure additive this curing temperature can be reduced to 225 degrees F. Low temperature curing is

preferred when fabrics with low melting points are used as the substrate (e.g., synthetic materials such as polyester or nylon).

Example

A retroreflective ink of the invention was prepared by mixing 3 parts of 409 AG REFLECTIVE CLEAR LF base (International Coatings Corporation, Cerritos, CA) with 1 part Grancill PWX binding and finishing agent (Grant Industries, Elmwood Park, NJ 07407). 409 AG REFLECTIVE CLEAR LF base includes water as a volatile component, uncoated roughly spherical glass beads having a mean diameter of about 25 microns, and a matrix material. 409 AG Reflective Clear LF base is made by mixing approximately 2 pounds of uncoated roughly spherical glass beads into each gallon of a textile ink base sold by International Coatings Corporation (400 series Waterbase #402LF) and then adjusting the viscosity using a volatile component to approximately 0.090 to 0.110 centistokes (i.e., a specific gravity compatible with screen printing and for maintaining bead suspension). Grancill PWX includes water as a volatile component, binding agents that help adhere solid particle to a substrate, and finishing agents that facilitate the use of the ink in screen printing applications. CX100 cross link (Zeneca Industries) was then added in a quantity of 2% of the total volume. This ink was screen printed onto a fabric in a predetermined pattern. The printed fabric exhibited low daytime noticeability, while manifesting readily detectible retroreflectivity under low light conditions (e.g., under typical nightime lighting).

From the foregoing, it can be appreciated that the retroreflective inks and related methods of the invention provide compositions and processes for enhancing the visibility various objects under low visibility conditions.

Other Embodiments

While the above specification contains many specifics, these should not be construed as limitations on the scope of the invention, but rather as examples of preferred embodiments thereof. Many other variations are possible. Accordingly, the scope of the invention should be determined not by the embodiments illustrated, but by the appended claims and their legal equivalents.

Claims

What is claimed is:

1. A retroreflective ink comprising:

a non-volatile matrix material;

a volatile component; and

a plurality of beads;

wherein said beads lack a reflective coating.

2. The retroreflective ink of claim 1, wherein said beads have a mean diameter of about 10 to 40 microns.

3. The retroreflective ink of claim 2, wherein said beads have a mean diameter of about 25 to 35 microns.

4. The retroreflective ink of claim 2, wherein said beads have a mean diameter of less than 30 microns.

5. The retroreflective ink of claim 4, wherein said beads have a mean diameter of about 25 microns.

6. The retroreflective ink of claim 1, wherein said beads are colorless.

7. The retroreflective ink of claim 1, wherein said beads are tinted.

8. The retroreflective ink of claim 1, wherein said beads are solid.

9. The retroreflective ink of claim 1, wherein said beads comprise silica.

10. The retroreflective ink of claim 1, wherein said beads are roughly spherical in shape.

11. The retroreflective ink of claim 1, wherein said beads are not spherical.

12. The retroreflective ink of claim 1, wherein said volatile component consists essentially of water.

13. The retroreflective ink of claim 1, wherein said beads comprise about 55-60% the ink volume when all of the volatile carrier has been removed from the ink.

14. The retroreflective ink of claim 1, wherein the non-volatile matrix material comprises about 40-45% of the ink volume when all of the volatile carrier has been removed from the ink.

15. The retroreflective ink of claim 1, wherein the non-volatile matrix material comprises an acrylic copolymer.

16. The retroreflective ink of claim 1, wherein the volatile component, comprises about 45-50% by volume of said retroreflective ink.

17. A retroreflective ink comprising:
a non-volatile matrix material;
a volatile component; and
a plurality of beads;
wherein the retroreflective ink does not comprise pigment particles.

18. A fabric comprising the retroreflective ink of claim 1.

19. A fabric comprising the retroreflective ink of claim 15.

20. A method of making a retroreflective fabric, said method comprising the step of printing a fabric with the retroreflective ink of claim 1.

21. A method of making a retroreflective fabric, said method comprising the step of printing a fabric with the retroreflective ink of claim 17.

22. A retroreflective ink comprising a mixture comprising 409 AG REFLECTIVE CLEAR LF base and Grancill PWX binding and finishing agent.

INTERNATIONAL SEARCH REPORT

Inter. ..ional application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C08K 3/40; C08L 31/02. 33/02; C09D 11/00. 11/10

US CL : 523/160; 524/494. 556. 847

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/160. 161; 524/494. 556. 847; 106/31.6. 31.28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and. where practicable. search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 5,543,177 A (MORRISON et al.) 06 August 1996 (06/08/96), col.1, lines 12-13, col.10, lines 38-40 and 59-61, col.11, lines 4-5, col.23, lines 4-8, 11, and 28-31, col.24, lines 27-28, col.25, lines 45-47, col.27, lines 14-15, and col.46, line 64-col.47, line 3.	1, 6, 8-10, 12, 17-18, 20-22 ---- 19
Y	US 3,099,637 A (NELLESSEN) 30 July 1963 (30/07/63), col.4, lines 44-47.	7
Y	US 5,620,775 A (LAPERRE) 15 April 1997 (15/04/97), col.3, lines 41-51 and col.9, line 60-col.10, line 21.	11

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,736,602 A (CROCKER et al.) 07 April 1998 (07/04/98), col.2, lines 9-10, 24-26, and 54-60, col.3, lines 8 and 33-36, col.3, line 63-col.4, line 50.	1-6, 8-10, 12-15, 17
Y	US 5,650,213 A (RIZIKA et al.) 22 July 1997 (22/07/97), col.8, lines 22-30.	16
Y	US 5,564,843 A (KAWAGUCHI) 15 October 1996 (15/10/96), col.3, lines 34-60.	1-3, 6, 8-10, 12, 15
Y, P	US 5,998,525 A (WANG et al.) 07 December 1999 (07/12/99), col.3, lines 32-36, col.4, lines 8-14, and col.6, line 64-col.7, line 38.	1-3, 6, 8-10, 12, 15
A	US 5,673,148 A (MORRIS et al.) 30 September 1997 (30/09/97)	1-22
A	US 4,263,345 A (BINGHAM) 21 April 1981 (21/04/81)	1-22

INTERNATIONAL SEARCH REPORT

Inte...ational application No.
PCT/US00/24291

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

EAST
search terms: retroreflective. ink. beads. microspheres. microbeads. spheroids. microspheroids. glass. s..ica. acrylic. matrix. non-volatile. water. Grancill PWX. AG Reflective Clear LX